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INTERACTION OF ATOMS WITH SURFACES

by

J. N. Smith, Jr. and W. L. Fite

FINAL REPORT

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FOREWORD

This report was prepared by the General Atomic Division of General Dynamics Corporation, San Diego, California, on Air Force Contract AF 49(638)-356, "Interaction of Atoms with Surfaces". Dr. Wade L. Fite was the General Atomic project manager and Mr. Milton Rogers was the AFOSR project officer for this contract.

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ABSTRACT

Experimental modulated atomic beam techniques, adapted for the study of gas-surface interactions, are summarized. The scope and purpose of research conducted, using these techniques, are outlined. Several types of interactions between molecules and atoms, at thermal velocities, and solid surfaces are discussed. In particular, the dissociation of H_2 on tungsten, the scattering of H_2 on nickel, and the chemical reaction between Cl_2 and nickel are mentioned. Various other experimental observations and measurements are catalogued. This report is intended to be a brief summary of research conducted under AF contract AF 49(638)-356 during the period April 1, 1958 through September 30, 1962, and serves to re-emphasize the power and versatility, as well as the difficulties, associated with the use of beam techniques in the study of surface interactions.

CONTENTS

I. INTRODUCTION

In the consideration of aerodynamic flight in a rarefied atmosphere (e.g., when the mean free path of the gas molecules in the surrounding atmosphere is comparable with the dimensions of the flight vehicle), it becomes necessary to inquire into the microscopic details of the individual interactions between the atoms and molecules of the ambient gas and the solid surface of the vehicle. As an example, consider the drag coefficient, C_D. At low altitudes C_D can be expressed in terms of the macroscopic properties of the atmosphere, such as viscosity, etc. In a rarefied gas, however, such a formulation is no longer possible. In its place one seeks to express the aerodynamic drag in terms of the details of the individual gas-surface interactions. Theoretical formulations of the problem, such as that of Shamberg[1], indicate that C_D can be determined from the thermal accomodation coefficient, α, and a knowledge of the angular distribution of gas particles scattered by the solid surface.

A large number of experiments on gas-surface interactions has been performed previously; however, there is a great deal of disagreement in the various experimental results reported in the literature. This is partially due to difficulty in determining the exact nature of the solid surface during an experiment. Also, earlier investigations usually employed the same general experimental techniques and the desired results were achieved by rather indirect means, such as from observation of the pressure drop in a flask or the temperature change of a filament immersed in a gas at low density. Many experiments have been performed with surfaces consisting of a single crystal face of the material under study, and, while the results of such work are important from a purely scientific standpoint, it is impossible to apply them to polycrystaline materials of engineering interest. It was with these points in mind that an experimental research program under AFOSR auspices was begun in April, 1958, to investigate gas-surface interactions as they affect the aerodynamics of the upper atmosphere.

During the past 4-1/2 years, the approach has been to apply modulated atomic-beam techniques to the study of the interaction of atoms and molecules with solid surfaces. Beam experiments offer several advantages over older methods. Perhaps most important is the fact that it is possible to observe directly the results of a single collision of a molecule with the surface. Angular distributions of scattered particles may be obtained by

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rotating a detector about a target surface placed in the path of the beam. Thermal accomodation coefficients are obtained by comparing the number density (inversely proportional to mean velocity) of the direct and scattered beams. When using partially-disassociated molecular beams, recombination coefficients may be derived from a comparison of the dissociation fractions of the incident and scattered beams. Mass spectrometric detection of the particles evolving from a surface exposed to a molecular beam provides information concerning possible chemical reactions occurring at the surface. The specific advantages that accrue from the use of modulation techniques will now be discussed.

From the foregoing remarks it becomes apparent that beam techniques provide a powerful analytical tool for the study of gas-surface interactions. However, until the research program was well under way, it was not realized just how powerful the technique was. Upon close examination, many unexpected phenomena were found to accompany the collision of an atom or molecule with a surface. Most of these phenomena could not readily be explained and, therefore, we deemed it imperative to deviate from the initial goals of the research program to search for explanations for these various observations. For this reason much of the research since 1959 has been of an exploratory nature with relatively little emphasis on the problems of aerodynamic drag in rarefied gases.

II. EXPERIMENTAL APPARATUS

2.1 VACUUM SYSTEM

The vacuum system of the modulated atomic beam apparatus utilized in these experiments consists of three differentially-pumped chambers. The first of these chambers contains the beam source which typically consists of a tungsten furnace or an rf gas discharge. The beam issuing from the source passes axially through the second, or buffer, chamber and then into the third, or experimental, chamber. The ultimate base pressure in this chamber is 2×10^{-7} mm Hg. The target surface and beam detector are located in the third chamber. Also in this chamber is a rotating, toothed, chopper wheel that interrupts the beam at the modulation frequency. The overall length of the beam from source to target is about 40 cm. The beam detector is mounted on a table that permits its rotation through 130 deg, about the point of intersection of beam and target, in the plane containing the incident beam and the target normal. The distance from the center of rotation to the detector is about 8 cm.

2.2 BEAM SOURCES

Two types of beam sources were utilized during most of the research. The first was a tubular tungsten furnace that could be heated over the range from 300°K to 3000°K. When using H_2 as the source gas, arbitrarily high dissociations could be obtained at high furnace temperature and low furnace pressure. The second source consisted of an rf gas discharge. The discharge chamber was surrounded by a cooling jacket and the temperature of the beam was dictated by the temperature of the coolant, typically liquid N_2, CCl_4, or dry ice-acetone mixture. The rf discharge was used when a low temperature beam was desired. The rf discharge would provide dissociations of about 60 percent for H_2 and 30 percent for O_2.

In addition to these two basic beam sources, which provide beams at thermal velocities, we undertook the development of a third type early in the research program. Here, the goal was to provide a beam of oxygen atoms in the energy range 1 to 10 ev, which corresponds to typical satellite speeds. The approach taken was to neutralize an O^+ ion beam by the charge transfer reaction $O^+ + H \rightarrow H^+ + O$. Fast neutral beams were obtained; however, the resulting beam intensity was not large enough to be useful in a scattering experiment.

To examine the interaction of two gas species at a surface, a dual beam configuration, in which gas of one species was directed at the target surface in the normal modulated beam was used. The second gas

was introduced in a gross dc beam through a small tube placed about 3 cm from the target and aimed directly at it. Reaction products, if any, then occurred at the modulation frequency of the incident modulated beam and with a definite phase reference with respect to it.

In certain cases, it was desired to examine the results of a particle-surface collision without reference to the angle of incidence of the incoming particles or to the residence-reaction time of the particles at the surface. (The effect of long residence-reaction times on modulated signals ismentioned in Section 2.5.) To accomplish this, the target surface was positioned on the axis of the machine in the source chamber and the gas under study was introduced directly into this chamber. In this isotropic configuration, the current density of gas incident on the target was independent of angle. Gas particles leaving the target, in the direction of the target normal, passed through the buffer chamber and into the experimental chamber where they were modulated and detected in the same fashion as a normal beam.

2.3 TARGET MOUNTS

Three types of target holders were utilized in the course of this research. For studies at high surface temperatures, targets were constructed from metal foil and were mounted between water-cooled copper electrodes. The targets were then heated by applying low voltage ac to the electrodes. For surface temperatures below room temperature, targets were connected by a copper rod to a liquid nitrogen cooled surface. A heating filament was placed at the junction between the target and the rod to heat the target over the range from 77°K to ~800°K. In the third type of mounting, the target surface was mounted on one arm of a torsion balance and from the deflection of the balance, when it was placed in the incident beam, the momentum transfer could be derived.

2.4 SIGNAL DETECTION

In all of the experiments, mass spectrometric detection of the incident and scattered particles was employed. Ionization of neutral particles was achieved by electron impact ionization, yielding ion signals proportional to the number density, n, of neutral particles in the beam. Under certain conditions, it was necessary to measure the current density, J, of the beam. To accomplish this, an ac stagnation detector was constructed as an integral part of the neutral beam ionizer.[2]

The ion beam emerging from the neutral beam ionizer was mass analyzed in a 180 deg magnetic sector and detected with an electron multiplier. A narrow band amplifier tuned to the modulation frequency

provided further amplification. Phase sensitive rectification was accomplished by a mechanical chopper driven by a signal derived from a photocell mounted on the chopper wheel. A Leeds and Northrup chart recorder provided the final display of the signals. The electronic system used in these experiments is described fully elsewhere.[3,4]

2.5 COMMENTS ON MODULATION TECHNIQUES

Two advantages accrue from the use of modulation in these experiments. First is the great improvement in the signal-to-noise ratio resulting from the use of beams of non-condensible gases. This improvement results from the fact that the signals associated with the beam will occur at the fundamental of the chopping frequency (the higher harmonics are rejected by the narrow-band amplification) and will have a definite phase reference with respect to the passage of this beam through the chopper wheel, whereas noise arising from background gas signals will occur at all frequencies and in random phases. Phase-sensitive detection allows the beam signals to be discriminated from the noise thus generated.

The second advantage results from the fact that the phase-angle leads or lags between various signals are related to the time delay between the production of these signals at the neutral beam detector. This feature allows the reaction-residence time for a gas-surface interaction to be determined by making a comparison of the phase of the signal derived from particles incident upon the surface with the phase of the signal from the reaction products evaporating from the surface.

An analysis shows that if particles remain at a surface for a mean time τ before evaporation, and, if τ is large compared with the period of modulation, then phase reference is lost and the signal amplitudes become vanishingly small. The bulk of the research work was performed with a modulation frequency of 100 cps. At this frequency, a phase shift of 5 deg (the smallest resolvable) corresponds to a time delay of 140 μsec. Toward the end of the contract period, modulation at 1440 cps was used to extend this lower limit to ~ 10 μsec.

III. EXPERIMENTS

As mentioned previously, a great deal of the research has been of an exploratory nature and has attempted to explain certain apparently anomalous experimental observations. This is, of course, in addition to various investigations that have been completed and which yielded results of a reliable and useful nature. In the following sections, certain of the more interesting studies carried out in the past 4-1/2 years are discussed in chronological order. Less emphasis has been given to research carried out to a point warranting publication in the literature. In these latter cases, appropriate references are given.

3.1 IONIZATION OF ATOMIC OXYGEN

Since much of the research under this contract was to have been concerned with the interaction of atomic oxygen with a surface, and since ionization of neutral particles on electron impact was to be utilized, it was necessary to first determine the cross section for the reaction $e + o \rightarrow o^+ + 2e$. This measurement was completed in the early stages of the program and the results were published.[5]

3.2 TORSION BALANCE EXPERIMENTS

A torsion balance was constructed to make direct observations of momentum transfer to a surface under bombardment by a molecular beam. The balance consisted of a horizontal glass rod suspended from its center by a thin tungsten wire. Target surfaces were mounted at opposite ends of the rod to allow comparison of the characteristics of two surfaces to be made. Deflection of the balance was detected by means of a mirror, mounted on the balance, and a light source. Representative results obtained with this device were also published.[6]

3.3 MEASUREMENTS OF THERMAL ACCOMODATION COEFFICIENTS

The thermal accomodation coefficient, α, is expressed as

$$\alpha = (T_B - T_S)/(T_T - T_S)$$

where T_B is the kinetic temperature of the scattered beam, T_S is the incident beam temperature, and T_T is the target temperature. By monitoring the scattered beam signal as a function of T_S and T_T, T_B may be deduced and therefore α may be calculated. The mathematical details of this technique are discussed in reference (2). Certain of the results have been published.[6,7] α was also measured for H_2, N_2, O_2, and Ar on copper over the

temperature range from 95°K to 800°K. Generally, it is found that α increased with the mass of the incident molecule and, for a given molecule, decreased with increasing surface temperature. However, as emphasized by more recent observations, it is not clear how these earlier results should be interpreted; e.g., the nature and effects of adsorbed gas layers on the target surface is not adequately known. Example of side effects resulting from adsorbed gases will be discussed in Section 3.4.

3.4 PROBABILITY OF REFLECTION OF ATOMS

The probability of reflection was defined as $p = 1-p_d$ where p_d is the probability for the occurrence of processes giving rise to the disappearance of atoms; i.e., surface recombination or adsorption for a mean time that is long compared with the period of modulation. The probability p was determined experimentally by comparing the incident and reflected atomic beam signals and applying the appropriate geometrical correction. For this phase of the research, the rf discharge source was used.

p was determined for H and O on copper, silver, aluminum, polyethylene, Teflon, and Pyrex. It was found that p was remarkably insensitive to the material from which the target was constructed. The result for Pyrex was particularly disturbing. From the work of others, it was expected that p should approach 1; however, for H on Pyrex, p was found experimentally to be about 0.8.

An internally-baffled chamber was constructed of copper so that a particle entering at one end would be required to undergo multiple collisions with the interior walls of the chamber before emerging at the opposite end. A partially-dissociated beam of H_2, issuing from the rf discharge source, was examined mass-spectrometrically before entering the chamber, as was the gas emerging from the opposite end of the chamber. It was found that the probability for an atom to pass through the chamber unaltered was sensibly the same as that obtained for the probability of reflection of an H atom on a single collision, as determined with a standard copper target. This result still is not understood.

One may take as a working hypotheseis that the preceeding result was associated with the difference between adsorbed gas layers on the surface directly exposed to the emanations from the rf discharge beam source and the adsorbed gas layers on the surfaces hidden from the view of the beam source. Using this hypothesis, a study was conducted on the phenomena which occurred when a surface with an adsorbed gas layer was exposed to the products of an rf discharge. It was found that, above about 150°K (the "freeze-out" temperature for H_2O at these pressures), modulated signals occurred at the mass

number corresponding to the species introduced into the chamber via the dc beam. Various tests and theoretical considerations indicated that molecules in excited vibrational stages, issuing from the discharge, were responsible for the desorption of gas particles lodged on the surface. This effect was not noted when the furnace source was used.

To follow through with the diagnostic study of the interactions of H atoms with surfaces, particular interest was given to a study of the reaction $H + D_2 \rightarrow HD + D$ occurring on a nickel surface. This reaction is chemically similar to the reaction $H + H_2 \rightarrow H_2 + H$, however the detection of the latter reaction is complicated by the fact that both the reactants and the products have the same mass. The former reaction was found to occur with a high efficiency at surface temperatures above 700°C. Below 700°C, only vanishingly small amounts of HD were detected. From the extensive studies of this reaction in the literature it is known that the process $H + D_2 \rightarrow HD + D$ has a very small activation energy on clean nickel. It seems probable, therefore, that the minimum temperature at which the $H + D_2$ reaction occurs is associated with the evolution of adsorbed gases from the nickel surface, and that very likely the other phenomena mentioned are due to adsorbed gas effects. This observation leads to one of the experimental difficulties of gas-surface research; that is, very close attention must be given to the effects of adsorbed gas layers in the measurement of the various parameters describing the interaction.

In using reflected beam techniques, detection sensitivity requires that relatively intense beams must be utilized. Under these conditions, the surface will "dirty-up", through adsorption, with gas of the beam species, under many of the surface and temperature conditions that one would like to investigate. This will occur, of course, even under ultra-high vacuum conditions.

3.5 OTHER CHEMICAL REACTIONS

The success obtained in observing the hydrogen-deuterium exchange reaction prompted us to survey other surface-catalyzed chemical reactions involving simple molecules. Certain of the reactions that were observed are itemized as follows:

$$(1)\ D_{ac} + H_2O_{dc} \rightarrow HDO_{ac}$$

$$(2)\ D_{ac} + CO_{dc} \rightarrow D_2O_{ac}$$

$$(3)\ D_{ac} + NO_{dc} \rightarrow D_2O_{ac}$$

$$(4)\ D_{ac} + O_{2_{dc}} \rightarrow D_2O_{ac}$$

(5) Formation of nickel chlorides

(6) Desorption of CO from Ni

In the first four reactions, the subscripts on the left indicate whether the reactant was introduced via the modulated (ac) beam or the gross (dc) beam. The target surface was nickel in all cases. Only the products detected as modulated signals are indicated on the right hand side. A mass sweep failed to yield signals other than those indicated.

The fifth reaction, the formation of nickel chlorides, is discussed in Reference (2). With the normal beam configuration, Cl_2 was directed at a heated Ni target and NiCl was detected with a phase shift with respect to the incident Cl_2 which was indicative of a reaction-residence time of 900 μsec at 1100°C, decreasing to less than 200 μsec at 1300°C. In the isotropic source configuration, $NiCl_2$ was observed above 600°C.

In the sixth reaction, it was found that modulated CO signals could be observed if a heated nickel target was exposed to ac beams of O_2, N_2, NO, and, surprisingly, Ar. CO was not observed with beams of H_2 or He. The origin of the CO is not known, particularly with respect to argon. It was found, however, that after a given target was heat cycled for several hours, CO signals were no longer observed. Other anomolous effects apparently due to carbon impurities in nickel are described in Reference (2).

3.6 DISSOCIATION OF H_2 ON TUNGSTEN

The results of this experiment have been published.[7] In summary, the probability of dissociation of H_2 on W was found to be temperature independent at a value of 0.3 above 2500°K. Also, while the angular distribution of scattered H_2 obeyed the cosine law, indicative of diffuse reflection at low W temperatures, a shift toward specular scattering was noted at 2500°K. At this temperature the angular distribution of H_1 evaporating from the target was diffuse.

3.7 SCATTERING OF H_2 AT A NICKEL SURFACE

These experiments are discussed in Reference (2). Again, to summarize, a marked temperature dependence was noted in the angular distribution of H_2 scattered by a nickel target. Below about 150°C and above 700°C, the scattering was diffuse. However, in the range between these temperatures, the scattering became strongly peaked in the region of the specular angle. Numerous experiments suggested that a carbon impurity was responsible for these effects. Of particular interest was the determination that the thermal accomodation coefficient is apparently angular-dependent.

IV. CONCLUSIONS

As indicated earlier, molecular beam techniques provide a powerful approach to the study of gas-surface interactions, and this very power implicit in the method has proven to be both the boon and the bane of the research carried out under this contract. The basic appeal of a reflected beam experiment, particularly using modulation techniques and mass-spectrometric detection, is that, in such an experiment, phenomena are isolated much better than in most other gas-surface experiments and microscopic rather than macroscopic information is obtained. Generally speaking, the experiments have proven to be quite successful in this regard, since in many instances specific phenomena have been observed and studied with a high degree of freedom from other effects which normally tend to obscure them. The experiments are, in principle, much simpler to interpret than most others in this area.

At the same time, the power of the method to isolate phenomena has resulted in the appearance of a great number of effects which have been totally obscured in past experiments using less sophisticated techniques. In consequence, interpretational difficulties attend these experiments as well as others, but the problem has changed character. Rather than needing to extract information regarding a particular process from data which has been averaged in the experiments (as is the case with more conventional studies), the problem associated with beam experiments is the handling and consolidation of the large amount of detailed microscopic information which is the output of a reflected beam experiment.

As indicated in this report, at the present time reflected beam research has presented a great deal of information which is not understood within the framework of existing theory. Time has simply not been adequate to investigate fully many of the most interesting and potentially most significant phenomena. There would seem little doubt that those phenomena, which have been adequately isolated and studied sufficiently under this contract to warrant publication, do represent significant contributions to the field and that continuing effort in this research will continue to present sound and, perhaps surprising, results of direct importance to problems of hypersonic flight as well as to other fields.

REFERENCES

Of the following references, numbers 2, 5, 6, and 7 are publications resulting from work done under this contract. Reference 3 describes work performed using the techniques developed under this contract.

1. R. Schamberg, "Analytic Representation of Surface Interation for Free-Molecule Flow with Application to Drag of Various Bodies," Rand Corporation Report R-339, section 12, 2nd printing, February, 1962.

2. Joe N. Smith, Jr., and Wade L. Fite, "Recent Investigations of Gas-Surface Interactions Using Modulated-Atomic-Beam Techniques." To be published in the Proceedings of the Third International Symposium on Rarefied Gas Dynamics, Academic Press.

3. R.T. Brackmann and W. L. Fite, "Condensation of Atomic and Molecular Hydrogen at Low Temperatures," J. Chem. Phys. 34, 1572 (1961).

4. W. L. Fite and R. T. Brackmann, "Collisions of Electrons with Hydrogen Atoms, I. Ionization," Phys. Rev. 112, 1141 (1958).

5. W. L. Fite and R. T. Brackmann, "Ionization of Atomic Oxygen on Electron Impact," Phys. Rev. 113, 815 (1959).

6. G. S. Holister, R. T. Brackmann, and W. L. Fite, "The Use of Modulated Atomic Beam Techniques for the Study of Space Flight Problems," AFOSR-TN 59-1033. Also published in Proceedings of a Conference on Physical Chemistry in Aerodynamics and Space Flight, Pergamon Press, p. 162 (1960).

7. Joe N. Smith, Jr., and W. L. Fite, "Reflection and Dissociation of H_2 on Tungsten," J. Chem. Phys. 37, 898 (1962). Also Air Force Technical Note, AFOSR 2611 (General Atomic Report No. GA-3009).

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